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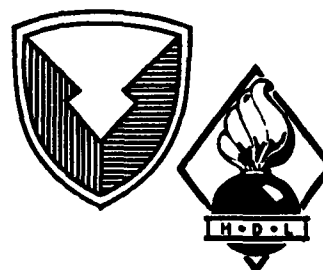
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# Host Materials for $4d^N$ and $5d^N$ Transition-Metal Ions

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This report discusses ten compounds which are potential host materials for quadruply ionized elements with $4d^N$ and $5d^N$ electronic configurations. These compounds are $ZrSiO_4$, $HfGeO_4$, $Li_2ZrTeO_6$, $Li_2HfTeO_6$, $Li_6BeZrF_{12}$, $ZrGeO_4$, $ZrGeO_8$, $ThSiO_4$, and $ThGeO_4$ (in two forms: zircon and scheelite). The crystal-field components, $A_{nm}$, are calculated for the Zr, Hf, and Th sites in each of the compounds. The site symmetry is $S_4$ or $D_{2d}$, except for $Li_2XTeO_6$ ($X$ = Zr, Hf) which has $C_3$ symmetry. Approximate parameters, $F^{(k)}$, $B_{nm}$ ($B$, $C$, $Dq$), are given for the entire quadruply ionized $5d^N$ configuration. Energy levels of $W^{4+}$ ($5d^2$) and $Re^{4+}$ ($5d^3$) are given for some compounds.

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# 1. Introduction

The spectra of the $4d^N$ and $5d^N$ electronic configurations are very limited, both in the solid state and the free ion. This is unfortunate since these ions have a number of levels in the infrared and visible spectral regions; because of the various ionization possibilities of each ion, they offer a rich area for possible tunable laser sources.

We wish to investigate the spectra of the $4d^N$ and $5d^N$ quadruply ionized ions in transparent oxide host crystals. This report provides the information we have found concerning these ions and presents a number of host materials which we consider candidates for immediate study.

The situation concerning the $4d^N$ and $5d^N$ transition-metal ions before 1962 is summarized by Ballhausen (1962). More recently, several of the $4d^N$ and $5d^N$ ions have been reported in fluoride or chloride host materials (Morrison, 1989). In this latter reference, six host materials are given for which experimental data have been reported on $4d^N$ and $5d^N$ ions. Unfortunately, in all these hosts, the electric dipole transitions are forbidden by the symmetry of the site occupied by the $4d^N$ or $5d^N$ ion. Consequently, the weak magnetic dipole transitions must be sorted out from relatively strong vibronic transitions. Although this procedure can be done, it directs time and effort away from understanding the crystal-field splitting and developing a model for these splittings. Thus, time would be better spent selecting a host material that does have electric dipole transitions allowed for the site occupied by the $4d^N$ or $5d^N$ ions.

We have selected several host materials in which $Hf^{4+}$, $Zr^{4+}$, or $Th^{4+}$ is a constituent that can be replaced substitutionally by a quadruply ionized $4d^N$ or $5d^N$ ion; also, the site occupied by these ions allows electric dipole transitions. In addition, we have selected hosts with the site symmetry high enough for us to analyze ($C_3$, $C_4$, and higher) with our present programs. A number of these materials have either $Si^{4+}$ or $Ge^{4+}$ as constituents, and crystal-field components have been calculated for these sites. These sites can be occupied by quadruply ionized $3d^N$ ions, and experimental data have been reported on $V^{4+}$ in several zircon-type crystals considered here (Di Gregario et al, 1982).

Unfortunately, for the hosts we have chosen, the available data are only x-ray data and some crystal growth data, with no experimental data on $4d^N$ and $5d^N$ optical spectra. The $4d^N$ and $5d^N$ transition elements have not been tried as potential lasers possibly because so little experimental data have been taken and their spectra have not been identified. That is, for these ions, we have no method of simply analyzing the experimental data, such as the Tanabe-Sugano diagrams,

which have been so successful for the analysis of the $3d^N$ series spectra. We now have available Tanabe-Sugano-like diagrams for the $4d^N$ and $5d^N$ electronic configurations, which include the large spin-orbit coupling necessary in the analysis of the spectra of these ions. We intend to publish these diagrams in the near future, including the diagrams of quadruply ionized $5d^N$ ions for tetrahedral symmetry ($Dq/B < 0$), which can be used with the cubic approximation given in this report to predict the spectra of these ions in the host materials considered here.

# 2. Crystallographic Data and Crystal-Field Components

The tables in the appendix contain the crystallographic and x-ray data on each host. The arrangement of the tables is the same as in Morrison (1989); a detailed discussion of the arrangement is given on page 24 of that reference. These data are used to compute the crystal-field components for a particular site and reflect the symmetry of the site. In the discussion here we use only the monopole crystal-field components; the other contributions to the crystal field are included in anticipation of future possible refinements in the analysis. The crystal-field parameters are given by

$$B_{nm} = \rho_n A_{nm} ,$$  (1)

where the $\rho_n$ are "effective" values of $<r^n>$ for a particular ion in the solid. The $A_{nm}$ are given in the tables by Morrison (1989). Since we have no experimental data on these ions in the hosts considered here, we defer the derivation of approximate values of $\rho_n$ until later. The tables on each host are followed by the references to the data given on that host, so that in a certain sense each host material is a complete and separable item.

# 3. Hamiltonians for $d^N$ Electronic Configuration in a Crystal

## 3.1 Free-Ion Hamiltonian

The free-ion Hamiltonian for a configuration of $d^N$ electrons is taken as

$$H_{FI} = F^{(2)}g_2 + F^{(4)}g_4 + \zeta \sum_{i=1}^{N} \vec{l_i} \cdot \vec{s_i} ,$$  (2)

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with

$$g_k = \sum_{i>j} \sum_{q=-k}^{k} C^*_{kq}(i) \; C_{kq}(j) \; , \tag{3}$$

$$C_{kq} = \sqrt{4\pi/(2k + 1)} \; Y_{kq} \; . \tag{4}$$

The $F^{(k)}$ and $\zeta$ have been calculated by using Hartree-Fock wavefunctions (Morrison, 1989), and the matrix elements of $g_k$ are given by Neilson and Koster (1963). Frequently the Racah parameters $B$ and $C$ are used in place of the Slater parameters, $F^{(k)}$; the relations (Morrison, 1989, p 29)

$$\begin{aligned} F^{(2)} &= 7(7B + C) \; , \\ F^{(4)} &= (63/5) \; C \; , \end{aligned} \tag{5}$$

can be used to convert from one set of parameters to the other.

In general, the Slater parameters are considerably reduced when the ion enters a solid. Furthermore, these same parameters obtained by fitting the free-ion spectra are less than the corresponding values computed with Hartree-Fock wavefunctions. For example, for $Cr^{3+}$ we obtained the following values (Morrison, 1989, pp 21, 14, and 119):

| Parameter | Hartree-Fock calculation | Free-ion experiment | $Al_2O_3$ experiment |
|---|---|---|---|
| $F^{(2)}$ | 88,514 | 74,201 | 53,690 |
| $F^{(4)}$ | 55,558 | 45,822 | 39,312 |
| $B$ | 1,177 | 994.7 | 650 |
| $C$ | 4,409 | 3,637 | 3,120 |

We see that $B$ decreases from the Hartree-Fock value to the value obtained for $Cr^{3+}$ in $Al_2O_3$. Further, $Dq$ for $Cr^{3+}$ is 1596 cm$^{-1}$, so that $Dq/B = 2.56$. On the other hand, we can compute the $Dq$ using $<r^4>$ from Hartree-Fock values and the crystal-field component, $A_{40}$. Using equation (1), we obtain $Dq = 439.9$ cm$^{-1}$ and $Dq/B = 0.374$, which is considerably less than the value of $Dq/B = 2.56$ observed in experiment. $Dq/B$ is one of the fundamental quantities extracted from experimental data using a standard Tanabe-Sugano plot. We find that the Hartree-Fock method greatly underestimates the values of $Dq/B$, compared to experimental data. This is not surprising, since the value of $B$ decreases significantly when an ion enters the solid, whereas the radial wavefunction of the transition-metal ion expands, causing an increase

of $<r^4>$. These two effects cause the ratio $Dq/B$ to increase dramatically.

## 3.2 Crystal-Field

The crystal-field Hamiltonian appropriate for $S_4$ and $D_{2d}$ symmetry for the electronic configuration $d^N$ can be written as

$$H_{CEF} = B_{20} \sum_{i=1}^{N} C_{20}(i) + B_{40} \sum_{i=1}^{N} C_{40}(i) + B_{44} \sum_{i=1}^{N} \left[ C_{44}(i) + C_{4-4}(i) \right], \quad (6)$$

with the crystal-field parameters $B_{nm}$ real (Morrison, 1989). Actually the crystal-field Hamiltonian given in equation (6) is valid for the electronic configuration $d^N$ for site symmetries as low as $C_4$ with $B_{nm}$ real. If the site occupied by the ion has cubic symmetry, then $B_{20} = 0$, $B_{44} = (5/14)^{1/2} B_{40}$, and equation (6) becomes

$$H_{CEF}^{C} = B_{40}^{C} \sum_{i=1}^{N} \left\{ C_{40}(i) + \sqrt{\frac{5}{14}} \left[ C_{44}(i) + C_{4-4}(i) \right] \right\}. \quad (7)$$

In equation (7) if $B_{40} > 0$, then we have octahedral symmetry, and if $B_{40} < 0$, we have tetrahedral symmetry. In both cases, the crystal-field parameter $B_{40}$ is related to $Dq$ by

$$B_{40}^{C} = 21 \, Dq \ . \quad (8)$$

Here, the experimentally determined $Dq$ is often taken positive, and the sign of $B_{40}$ in equation (8) is determined by additional knowledge of the symmetry of the particular site. In the cases considered here, the sign of $B_{40}$ will be taken to be the same as the monopole crystal-field component, $A_{40}$.

Frequently, it is convenient to assume that the symmetry of the site occupied by the transition-metal ion is approximately cubic and use the rotational invariant (Leavitt, 1982) given by

$$S_4(B) = \sqrt{B_{40}^2 + 2B_{44}^2} \quad (9)$$

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to obtain a value of the crystal-field parameters, $B_{40}^C$, as

$$B_{40}^C = \sqrt{\frac{7}{12}}\, S_4(B) \quad .$$  (10)

Here we have used the result

$$S_{40}^C(B) = \sqrt{\frac{12}{7}}\, B_{40}^C \quad ,$$  (11)

$$B_{44}^C = \sqrt{\frac{5}{14}}\, B_{40}^C \quad .$$  (12)

The sign of $B_{40}^C$ in equation (10) must be determined from additional information on the particular site occupied by the transition-metal ion. If detailed x-ray data are available on a particular host material, the crystal-field components, $A_{nm}$, can be computed and equation (1) used to obtain

$$B_{40}^C = \sqrt{\frac{7}{12}}\, \rho_4 \, S_4(A)$$  (13)

from equation (11). The sign of $B_{40}^C$ given in equation (11) is then the same as $A_{40}$. The cubic approximation is good only as long as $B_{20}$ (or $A_{20}$) ~ 0 and $B_{44}$ (or $A_{44}$) ~ $(5/14)^{1/2}\, B_{40}(A_{40})$.

If the site occupied by the transition-metal ion has $C_3$ symmetry or higher, the crystal-field Hamiltonian is

$$H_{CEF} = B_{20} \sum_{i=1}^{N} C_{40}(i) + B_{40} \sum_{i=1}^{N} C_{40}(i) + B_{43} \sum_{i=1}^{N} \left[ C_{43}(i) - C_{4-3}(i) \right] \quad ,$$  (14)

where, as before. all $B_{nm}$ are real.

The cubic approximation in this symmetry is given by

$$B_{20} = 0 \quad ,$$
$$B_{40}^C = \sqrt{\frac{10}{7}}\, B_{40} \quad ,$$  (15)

and

$$H_{CEF}^C = B_{40}^C \sum_{i=1}^{N} \left\{ C_{40}(i) + \sqrt{\frac{10}{7}} \left[ C_{43}(i) - C_{4-3}(i) \right] \right\} . \tag{16}$$

Also in this symmetry the relation

$$B_{40}^C = 14 \, Dq \tag{17}$$

relates the experimental $Dq$ to the crystal-field parameter $B_{40}$. The rotational invariant corresponding to equation (9) is given by

$$S_4(B) = \sqrt{B_{40}^2 + 2B_{43}^2} . \tag{18}$$

The approximate cubic field parameters corresponding to equation (10) are given by

$$B_{40}^C = \sqrt{\frac{7}{27}} \; S_4(B) , \tag{19}$$

$$B_{43}^C = \sqrt{\frac{10}{7}} \; B_{40}^C , \tag{20}$$

where we have used the result

$$S_4^C(B) = \sqrt{\frac{27}{7}} \; B_{40}^C . \tag{21}$$

In this cubic symmetry if $B_{40} < 0$, we have octahedral symmetry, and if $B_{40} > 0$, we have tetrahedral symmetry. The results given in equations (10), (12), (19), and (20) are sufficient for the ascent from $C_4$ and $C_3$ symmetry to cubic symmetry. Along with the relation

$$S_4(B) = \rho_4 S_4(A) , \tag{22}$$

we can determine the approp te approximate cubic representation for a site in a solid provided we i. ve detailed x-ray data on that solid. For particular solids where the site occupied by a transition-metal ion has low symmetry, such as $C_2$, the rotational invariant $S_2(A)$ can be used as well as $S_4(A)$ to approximate the site from a representation of higher symmetry. In section 4 the cubic approximation is considered for the

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sites assumed to be occupied by quadruply ionized $5d^N$ transition-metal ions in each of the hosts considered.

The method we have chosen of obtaining approximate values of the $F^{(k)}$ and $\rho_k$ values is to use the data obtained on the quadruply ionized ions of the $5d^N$ series ($Re^{4+}$, $Os^{4+}$, $Ir^{4+}$, and $Pt^{4+}$) (see table 28.3, p 133 of Morrison, 1989). These data were taken on the above four ions in $Cs_2GeF_6$ (Ge in $O_h$ symmetry). From the x-ray data we obtain a point charge value $A_{40} = 21,689$ cm$^{-1}$/($Å^4$), and from the experimentally determined $B_{40}$, we obtain an average value of $\rho_4 = 3.108 <r^4>_{II-F}$. Using the $F^{(k)}$ (Morrison, 1989, table 2, p 12), we obtain an average value $F^{(k)} = 0.649 F^{(k)}_{II-F}$. Using these values we obtain the results given in table 1 for the estimated parameters for the quadruply ionized ions of the $5d^N$ series. The values of $\rho_2$ used in constructing this table were obtained from $\rho_2 = 1.733 <r^2>_{II-F}$, as in Morrison and Turner (1988).

# 4. Cubic Approximation for Each Host

For each of the hosts given in the tables in appendix A, the appropriate cubic approximation is given below, using the monopole $A_{nm}$ given in the appendix for that host.

## 4.1 ZrSiO₄

For the Zr site in $ZrSiO_4$ the monopole crystal-field components, $A_{nm}$ (cm$^{-1}$/$Å^n$), are $A_{20} = -12,756$; $A_{40} = 910.3$; $A_{44} = 8,630$; and $S_4 (A) = 12,239$.

From equations (10) to (12), we have

$$B_{40}^C = 9347\ \rho_4\ ,$$
$$B_{44}^C = 9347\ \rho_4\sqrt{\frac{5}{14}}\ .$$

Since $A_{40} > 0$, we have chosen $B_{40}^C > 0$, and although the site symmetry is tetragonal ($D_{2d}$), the cubic approximation is octahedral. Actually for either octahedral or tetrahedral symmetry the relation $|A_{44}| \sim (5/14)^{1/2}|A_{40}|$ should prevail, which is obviously far from being a good approximation.

Using the values of $\rho_n$ from table 1, we calculated the crystal-field parameters $B_{nm}$ for $W^{4+}$ ($5d^2$) in the cubic approximation and for the Zr

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site in $ZrSiO_4$. The results are given in table 2a (cubic) and table 2b (Zr site). The parameters used in the calculation are given in each table. As can be seen, the energy levels are quite distinct and, in particular, the composition of the ground state is quite different—in the cubic approximation the ground state has 4 percent $^3P$, which is completely missing in the $D_{2d}$ symmetry. Furthermore, the ground state becomes almost pure $^3F$ (97 percent) in the $D_{2d}$ symmetry. In both cases the spin-forbidden rule is invalid because of the admixture of the $^1D$ state into the Hund ground state by the strong spin-orbit interaction. Tables 2c and 2d present the cubic approximation and $D_{2d}$ calculation, respectively, for $Re^{4+}$ ($5d^3$) in the Zr site in $ZrSiO_4$. The results show that the cubic approximation is not good and in the analysis of experimental data, one should proceed directly from the $D_{2d}$ analysis since the cubic approximation could be misleading.

## 4.2 HfGeO$_4$

For the Hf site in $HfGeO_4$ the monopole crystal-field components, $A_{nm}$ (cm$^{-1}$/Å$^n$), are

$$A_{20} = 6465, A_{40} = -706.6, |A_{44}| = 4663, \text{ and } S_4(A) = 6632 \ .$$

Then, as above,

$$B_{40}^C = -5056\, \rho_4 \ ,$$
$$B_{44}^C = -5056\, \rho_4 \sqrt{\frac{5}{14}} \ .$$

With $A_{40} < 0$, we have tetrahedral symmetry. However, as in $ZrSiO_4$, the cubic representation is a poor one.

## 4.3 Li$_2$XTeO$_6$ (X = Zr, Hf)

For the Zr site in $Li_2ZrTeO_6$, the monopole crystal-field components (cm$^{-1}$/Å$^n$) are

$$A_{20} = 457, A_{40} = -14,546, |A_{43}| = 18,247, \text{ and } S_4(A) = 29,622 \ .$$

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From equations (17) and (18) we have

$$B_{40}^C = -15{,}083\,\rho_4 \; ,$$

$$B_{43}^C = -15{,}083\,\rho_4\,\sqrt{\frac{10}{7}} \; .$$

Since $B_{40}^C < 0$ in this cubic representation, the site is approximately octahedral. In this case $|A_{43}| \sim (10/7)^{1/2}\,|A_{40}|$, and the approximation is a good one. Also, because $A_{20} \sim 0$, the approximation is even better. However, since the oddfold fields $A_{10}, A_{30}, A_{33}, A_{50}$, and $A_{53}$ are not negligible, the electric dipole transitions should be observable. We omit the details of the Hf site in $Li_2HfTeO_6$, since the results are very similar. However, since the spectra can be interpreted in terms of cubic symmetry and electric dipole transitions can be observed, this would probably be an excellent host.

To show the additional splitting in going from the cubic approximation to the correct symmetry in this host, we have used the above relation for the calculation of the energy levels of $W^{4+}$ in the Zr site in this host. The results are given in tables 3a (cubic) and 3b ($C_3$). By comparing the results, we see that the reduction from cubic to $C_3$ for this host introduces what might be referred to as fine structure on the cubic field splittings. Thus, the assertion that the spectra can be interpreted in terms of the cubic approximation appears valid.

## 4.4    $Li_6BeZrF_{12}$

$Li_6BeZrF_{12}$ is the only fluoride host, and judging from the results of $3d^N$ in fluoride hosts, the point-charge (monopole) model should be a good approximation. For the Zr site in $Li_6BeZrF_{12}$, the monopole crystal-field components, $A_{nm}$ (cm$^{-1}$/Å$^n$), are

$$A_{20} = 1411, \; A_{40} = -3101, \; A_{44} = 5393, \text{ and } S_4(A) = 9098 \; .$$

From equations (10) to (12) we have

$$B_{40}^C = -6949\,\rho_4 \; ,$$

$$B_{44}^C = -6949\,\rho_4\,\sqrt{\frac{5}{14}} \; .$$

(Taking the value of $B_{44}$ as positive or negative has no effect on the energy levels, just on the phase factors in the wave functions. However,

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letting $B_{44} \rightarrow -B_{44}$ corresponds to a rotation of $\pm 45°$, and this rotation must be used in the evaluation of $A_{32}$ and $A_{52}$ in any crystal-field model.) Since the relation $|(A_{44})| \sim (5/14)^{1/2} |A_{40}|$, the cubic approximation can be used to advantage in the analysis of the experimental data. However, $A_{20}$ is not negligible in this case, and its effects will probably be observable in the refinement of the experimental data. $Li_6BeZrF_{12}$ is certainly a host material that should be further investigated.

## 4.5 ZrGeO$_2$

The crystal-field components for the Zr site in $ZrGeO_4$ are

$$A_{20} = 5,175;\; A_{40} = -6,023, |A_{44}| = 7,484;\; \text{and } S_4(A) = 12,178 \; .$$

From equations (10) to (12), we have

$$B_{40}^C = -9301\, \rho_4 \;,$$

$$B_{44}^C = -9301\, \rho_4 \sqrt{\frac{5}{14}} \;.$$

However, since $(5/14)^{1/2}|A_{40}| = 3599$, we see that the cubic representation is not good ($A_{44}$ is approximately twice this value). Nevertheless, a rough first interpretation of the experimental data in terms of the tetrahedral cubic group might be tried.

## 4.6 Zr$_3$GeO$_8$

$Zr_3GeO_8$ has two sites for the Zr ions, but when the crystal is doped with quadruply ionized $5d^N$ ions, these ions may go preferentially into one of the two sites. The crystal-field components for the $Zr_1$ site are

$$A_{20} = 10,659;\; A_{40} = -7,875;\; A_{44} = 6,875;\; \text{and } S_4(A) = 12,512 \;.$$

For the cubic approximation we have

$$B_{40}^C = -9556\, \rho_4 \;,$$

$$B_{44}^C = -9556\, \rho_4 \sqrt{\frac{5}{14}} \;.$$

Again we have tetrahedral cubic symmetry but with the approximation rather poor: $A_{44} = -6875$, and $(5/14)^{1/2} |A_{40}| = 4706$. However, the

approximation is probably close enough to allow a first analysis of the experimental data.

For the $Zr_2$ site,

$$A_{20} = -7{,}440; \; A_{40} = -9{,}538; \; |A_{44}| = 8{,}910; \; \text{and} \; S_4(A) = 15{,}803 \; .$$

These results give

$$B_{40}^C = -12{,}070 \; \rho_4 \; ,$$

$$B_{44}^C = -12{,}070 \; \rho_4 \sqrt{\frac{5}{14}} \; .$$

As in the $Zr_1$ site, the tetrahedral cubic approximation is not very good but can be used in a preliminary analysis of the experimental data.

## 4.7  $ThSiO_4$

The crystal-field components for the Th site are

$$A_{20} = -6300, \; A_{40} = 18.45, \; A_{44} = 4906, \; \text{and} \; S_4(A) = 6938 \; .$$

The cubic approximation is

$$B_{40}^C = 5299 \; \rho_4 \; ,$$

$$B_{44}^C = 5299 \; \rho_4 \sqrt{\frac{5}{14}} \; .$$

However the cubic approximation is poor in this case and probably should not even be considered. For comparison with experimental data, on a particular ion, it would be better to use the parameters given in table 1 with the $A_{nm}$ given above to calculate the energy levels.

## 4.8  $ThGeO_4$

For $ThGeO_4$, the same procedure as for $ThSiO_4$ applies for the zircon form, but for the scheelite form

$$A_{20} = 3593, \; A_{40} = -3236, \; |A_{44}| = 5405, \; \text{and} \; S_4(A) = 8301 \; .$$

Then we have

$$B_{40}^C = -6340 \, \rho_4 \, ,$$

$$B_{44}^C = -6340 \, \rho_4 \, \sqrt{\frac{5}{14}} \, .$$

Since we have $|A_{40}| < |A_{44}|$, the symmetry is far from cubic, but again in a crude analysis of the experimental data, the tetrahedral cubic symmetry may work.

# 5. Conclusion

X-ray data have been given on nine possible host materials for the quadruply ionized ions with the $4d^N$ and $5d^N$ electronic configurations. Very little information on the crystal growth and physical properties of host materials is given; however, some information can be found in the references to the x-ray data. For $ZrSiO_4$, several references are given to the crystal growth. The x-ray data were used to obtain the crystal-field components, and the reported data on several quadruply ionized ions with the $5d^N$ electronic configuration were used to approximate the crystal-field parameters for any quadruply ionized ion in that series. Cubic approximates were made for each host material and shown to be quite poor for some of the hosts. For $W^{4+}$ ($5d^2$) in the Zr site in $ZrSiO_4$, explicit energy levels were calculated for the site in $D_{2d}$ symmetry and for the cubic approximation. For comparison, a similar calculation was performed for $Re^{4+}$ ($5d^3$). A second calculation made for $W^{4+}$ in the Zr site in $Li_2ZrTeO_6$ with $C_3$ symmetry showed the effect of a small trigonal distortion at the site.

Approximate values necessary to calculate the energy levels of all the quadruply ionized ions with the $5d^N$ electronic configuration are given (table 1) even though the ionization state of some of the ions may be difficult if not impossible to achieve. No similar detailed calculations were done on the $4d^N$ because the data necessary for an approximate calculation were unavailable.

Table 1. Approximate free-ion parameters (cm$^{-1}$) and values of $\rho_n$ (Å$^n$) for the quadruply ionized ions with the $5d^N$ configuration

| Ion | $nd^N$ | $F^{(2)}$ <br> $B$ | $F^{(4)}$ <br> $C$ | $\rho_2$ | $\rho_4$ |
|---|---|---|---|---|---|
| Ta | $5d^1$ | — <br> — | — <br> — | 1.732 | 5.757 |
| W | $5d^2$ | 41,947 <br> 537.8 | 28,071 <br> 2,228 | 1.539 | 4.244 |
| Re | $5d^3$ | 43,787 <br> 560.9 | 29,340 <br> 2,329 | 1.470 | 4.030 |
| Os | $5d^4$ | 45,558 <br> 583.3 | 30,556 <br> 2,425 | 1.278 | 2.865 |
| Ir | $5d^5$ | 47,364 <br> 606.0 | 31,804 <br> 2,524 | 1.206 | 2.530 |
| Pt | $5d^6$ | 48,754 <br> 624.0 | 32,725 <br> 2,597 | 1.127 | 2.183 |
| Au | $5d^7$ | 50,264 <br> 643.2 | 33,744 <br> 2,678 | 1.052 | 1.874 |
| Hg | $5d^8$ | 51,795 <br> 662.8 | 34,778 <br> 2,760 | 0.9697 | 1.554 |
| Tl | $5d^9$ | — <br> — | — <br> — | 0.8991 | 1.243 |

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**Table 2a. Energy levels of $W^{4+}$ in the Zr site of $ZrSiO_4$, cubic approximation[a]**

| Level | I.R.[b] | Energy $(cm^{-1})$ | Free ion state (%) | | | | | |
|-------|---------|--------------------|--------|---|--------|---|--------|---|
| 1 | $\Gamma_3$ | 0 | 88 $^3F$ | + | 4 $^3P$ | + | 3 $^1D$ | |
| 2 | $\Gamma_5$ | 471 | 84 $^3F$ | + | 8 $^3P$ | + | 6 $^1D$ | |
| 3 | $\Gamma_4$ | 5,202 | 86 $^3F$ | + | 13 $^3P$ | | | |
| 4 | $\Gamma_1$ | 6,243 | 70 $^3F$ | + | 21 $^3P$ | + | 4 $^1G$ | |
| 5 | $\Gamma_5$ | 10,972 | 41 $^1D$ | + | 40 $^1G$ | + | 18 $^3F$ | |
| 6 | $\Gamma_3$ | 11,829 | 45 $^1G$ | + | 43 $^1D$ | + | 7 $^3P$ | |
| 7 | $\Gamma_2$ | 20,101 | 99 $^3F$ | | | | | |
| 8 | $\Gamma_1$ | 21,013 | 33 $^1G$ | + | 30 $^1S$ | + | 21 $^3F$ | |
| 9 | $\Gamma_5$ | 21,302 | 86 $^3F$ | + | 6 $^1G$ | + | 4 $^3P$ | |
| 10 | $\Gamma_4$ | 22,239 | 91 $^3F$ | + | 4 $^3P$ | + | 3 $^1G$ | |
| 11 | $\Gamma_3$ | 22,591 | 88 $^3F$ | + | 8 $^3P$ | + | 2 $^1G$ | |
| 12 | $\Gamma_4$ | 27,406 | 80 $^3P$ | + | 14 $^3F$ | + | 4 $^1G$ | |
| 13 | $\Gamma_1$ | 27,409 | 61 $^3P$ | + | 27 $^1G$ | + | 7 $^3F$ | |
| 14 | $\Gamma_5$ | 27,930 | 41 $^3P$ | + | 33 $^1G$ | + | 15 $^1D$ | |
| 15 | $\Gamma_3$ | 30,612 | 76 $^3P$ | + | 17 $^3F$ | + | 5 $^1G$ | |
| 16 | $\Gamma_5$ | 32,666 | 46 $^3P$ | + | 30 $^1D$ | + | 15 $^1G$ | |
| 17 | $\Gamma_4$ | 33,399 | 91 $^1G$ | + | 7 $^3F$ | + | 1 $^3P$ | |
| 18 | $\Gamma_5$ | 42,252 | 93 $^3F$ | + | 3 $^1G$ | + | 2 $^1D$ | |
| 19 | $\Gamma_3$ | 50,460 | 51 $^1D$ | + | 44 $^1G$ | + | 2 $^3P$ | |
| 20 | $\Gamma_1$ | 61,007 | 61 $^1S$ | + | 35 $^1G$ | + | 2 $^3P$ | |

[a]The parameters are $F^{(2)} = 41,947$; $F^{(4)} = 28,071$; $\zeta = 3,102$; $B_{40} = 39,669$ $cm^{-1}$; and $B_{44} = (5/14)^{1/2} B_{40}$.

[b]Irreducible representations of the cubic $T_d$ group (Koster et al, 1963).

**Table 2b. Energy levels of $W^{4+}$ in the Zr site in $ZrSiO_4$[a]**

| Level | I.R.[b] | Energy (cm$^{-1}$) | Free ion state (%) | | | | | |
|---|---|---|---|---|---|---|---|---|
| 1 | $\Gamma_3$ | 0 | 97 $^3F$ | + | 2 $^1D$ | | | |
| 2 | $\Gamma_5$ | 929 | 92 $^3F$ | + | 5 $^1D$ | + | 1 $^1G$ | |
| 3 | $\Gamma_1$ | 2,917 | 80 $^3F$ | + | 12 $^1D$ | + | 5 $^1G$ | |
| 4 | $\Gamma_4$ | 3,047 | 75 $^3F$ | + | 14 $^1D$ | + | 9 $^3P$ | |
| 5 | $\Gamma_2$ | 7,295 | 98 $^3F$ | | | | | |
| 6 | $\Gamma_5$ | 7,679 | 97 $^3F$ | + | 1 $^3P$ | | | |
| 7 | $\Gamma_3$ | 8,358 | 93 $^3F$ | + | 4 $^3P$ | + | 2 $^1G$ | |
| 8 | $\Gamma_1$ | 10,726 | 45 $^3P$ | + | 40 $^3F$ | + | 6 $^1S$ | |
| 9 | $\Gamma_4$ | 10,831 | 43 $^3F$ | + | 41 $^1D$ | + | 13 $^3P$ | |
| 10 | $\Gamma_5$ | 11,222 | 71 $^3F$ | + | 18 $^3P$ | + | 6 $^1D$ | |
| 11 | $\Gamma_1$ | 12,106 | 41 $^1D$ | + | 28 $^1G$ | + | 19 $^3F$ | |
| 12 | $\Gamma_2$ | 14,536 | 72 $^3P$ | + | 27 $^3F$ | | | |
| 13 | $\Gamma_5$ | 14,634 | 37 $^3P$ | + | 29 $^1D$ | + | 17 $^3F$ | |
| 14 | $\Gamma_1$ | 14,772 | 55 $^3F$ | + | 22 $^1G$ | + | 20 $^3P$ | |
| 15 | $\Gamma_3$ | 14,975 | 50 $^3P$ | + | 27 $^3F$ | + | 12 $^1D$ | |
| 16 | $\Gamma_5$ | 16,247 | 44 $^1G$ | + | 29 $^3F$ | + | 13 $^3P$ | |
| 17 | $\Gamma_4$ | 17,044 | 60 $^1G$ | + | 15 $^3F$ | + | 15 $^3P$ | |
| 18 | $\Gamma_5$ | 21,962 | 66 $^1G$ | + | 18 $^3F$ | + | 10 $^1D$ | |
| 19 | $\Gamma_1$ | 21,992 | 75 $^1G$ | + | 14 $^3F$ | + | 6 $^3P$ | |
| 20 | $\Gamma_3$ | 22,005 | 37 $^1D$ | + | 34 $^1G$ | + | 24 $^3F$ | |
| 21 | $\Gamma_4$ | 23,169 | 34 $^1D$ | + | 34 $^1G$ | + | 19 $^3P$ | |
| 22 | $\Gamma_4$ | 32,071 | 75 $^3F$ | + | 23 $^3P$ | | | |
| 23 | $\Gamma_1$ | 32,443 | 46 $^1S$ | + | 23 $^3F$ | + | 16 $^1D$ | |
| 24 | $\Gamma_5$ | 32,507 | 80 $^3F$ | + | 13 $^3P$ | + | 6 $^1G$ | |
| 25 | $\Gamma_3$ | 34,991 | 47 $^3F$ | + | 31 $^3P$ | + | 17 $^1G$ | |
| 26 | $\Gamma_5$ | 35,837 | 73 $^3P$ | + | 22 $^3F$ | + | 3 $^1G$ | |
| 27 | $\Gamma_1$ | 35,894 | 63 $^3P$ | + | 14 $^3F$ | + | 11 $^1G$ | |
| 28 | $\Gamma_2$ | 37,107 | 51 $^3F$ | + | 27 $^1G$ | + | 21 $^3P$ | |
| 29 | $\Gamma_4$ | 39,165 | 79 $^3F$ | + | 18 $^3P$ | + | 1 $^1G$ | |
| 30 | $\Gamma_5$ | 39,590 | 66 $^3F$ | + | 30 $^3P$ | + | 3 $^1G$ | |
| 31 | $\Gamma_1$ | 40,269 | 52 $^3F$ | + | 44 $^3P$ | + | 1 $^1D$ | |
| 32 | $\Gamma_2$ | 42,169 | 72 $^1G$ | + | 22 $^3F$ | + | 5 $^3P$ | |
| 33 | $\Gamma_3$ | 44,998 | 44 $^1D$ | + | 37 $^1G$ | + | 9 $^3F$ | |
| 34 | $\Gamma_5$ | 45,830 | 52 $^1G$ | + | 35 $^1D$ | + | 6 $^3P$ | |
| 35 | $\Gamma_1$ | 74,204 | 42 $^1G$ | + | 35 $^1S$ | + | 20 $^1D$ | |

[a] *Parameters are $F^{(2)} = 41,947$; $F^{(4)} = 28,071$; $\zeta = 3,102$; $B_{20} = -19,631$; $B_{40} = 3,863$; and $B_{44} = 36,626$ cm$^{-1}$.*

[b] *Irreducible representation of the tetragonal group, $D_{2d}$. Koster et al (1963).*

## Table 2c. Energy levels of $Re^{4+}$ in the Zr site in $ZrSiO_4$, cubic approximation[a]

| Level | I.R.[b] | Energy $(cm^{-1})$ | Free ion state (%) | | | | |
|---|---|---|---|---|---|---|---|
| 1 | $\Gamma_8$ | 0 | 89 $^4F$ | + | 3 $^2D1$ | + | 3 $^2D2$ |
| 2 | $\Gamma_8$ | 9,397 | 25 $^2G$ | + | 20 $^4F$ | + | 16 $^2H$ |
| 3 | $\Gamma_8$ | 11,656 | 48 $^2G$ | + | 29 $^2H$ | + | 7 $^2P$ |
| 4 | $\Gamma_6$ | 12,804 | 33 $^2G$ | + | 24 $^2H$ | + | 23 $^2P$ |
| 5 | $\Gamma_7$ | 17,032 | 63 $^4F$ | + | 13 $^2D1$ | + | 8 $^2H$ |
| 6 | $\Gamma_8$ | 18,582 | 72 $^4F$ | + | 7 $^2G$ | + | 7 $^2H$ |
| 7 | $\Gamma_8$ | 20,027 | 73 $^4F$ | + | 9 $^2H$ | + | 7 $^4P$ |
| 8 | $\Gamma_7$ | 20,362 | 44 $^4F$ | + | 14 $^2D1$ | + | 13 $^2G$ |
| 9 | $\Gamma_6$ | 21,322 | 78 $^4F$ | + | 9 $^4P$ | + | 6 $^2P$ |
| 10 | $\Gamma_8$ | 22,457 | 27 $^4F$ | + | 21 $^2G$ | + | 20 $^2H$ |
| 11 | $\Gamma_6$ | 24,504 | 38 $^4P$ | + | 28 $^2G$ | + | 24 $^4F$ |
| 12 | $\Gamma_8$ | 26,505 | 45 $^4P$ | + | 22 $^2H$ | + | 15 $^4F$ |
| 13 | $\Gamma_7$ | 27,518 | 39 $^4F$ | + | 23 $^2H$ | + | 16 $^4P$ |
| 14 | $\Gamma_8$ | 28,717 | 42 $^4P$ | + | 39 $^4F$ | + | 9 $^2H$ |
| 15 | $\Gamma_6$ | 29,327 | 38 $^2G$ | + | 35 $^2H$ | + | 12 $^4P$ |
| 16 | $\Gamma_8$ | 30,583 | 30 $^2H$ | + | 19 $^4F$ | + | 16 $^2G$ |
| 17 | $\Gamma_7$ | 31,197 | 55 $^2G$ | + | 16 $^4P$ | + | 10 $^2H$ |
| 18 | $\Gamma_6$ | 32,498 | 52 $^2G$ | + | 21 $^4P$ | + | 15 $^2H$ |
| 19 | $\Gamma_8$ | 32,681 | 37 $^2H$ | + | 24 $^2G$ | + | 18 $^4F$ |
| 20 | $\Gamma_8$ | 35,005 | 28 $^2H$ | + | 27 $^2D2$ | + | 12 $^4F$ |
| 21 | $\Gamma_6$ | 36,207 | 29 $^2H$ | + | 28 $^2P$ | + | 23 $^2F$ |
| 22 | $\Gamma_8$ | 36,764 | 48 $^2H$ | + | 18 $^2F$ | + | 12 $^2G$ |
| 23 | $\Gamma_7$ | 37,755 | 31 $^2F$ | + | 20 $^2D2$ | + | 19 $^2H$ |
| 24 | $\Gamma_8$ | 39,768 | 35 $^2F$ | + | 28 $^2D2$ | + | 17 $^4P$ |
| 25 | $\Gamma_7$ | 41,848 | 95 $^2F$ | + | 1 $^2G$ | + | 1 $^2D2$ |
| 26 | $\Gamma_8$ | 42,605 | 39 $^4F$ | + | 25 $^4P$ | + | 12 $^2D2$ |
| 27 | $\Gamma_7$ | 42,770 | 36 $^4F$ | + | 34 $^4P$ | + | 16 $^2F$ |
| 28 | $\Gamma_8$ | 44,686 | 39 $^4F$ | + | 21 $^4P$ | + | 21 $^2F$ |
| 29 | $\Gamma_6$ | 45,627 | 57 $^4F$ | + | 17 $^2H$ | + | 14 $^4P$ |
| 30 | $\Gamma_8$ | 50,073 | 28 $^2D1$ | + | 23 $^2G$ | + | 20 $^2D2$ |

[a]The parameters are $F^{(2)} = 43,787$; $F^{(4)} = 29,340$; $\zeta = 3,741$, $B_{40} = 37,668$ $cm^{-1}$; and $B_{44} = (5/14)^{1/2} B_{40}$.

[b]Irreducible representations of the double cubic group, $T_d$ (Koster et al, 1963).

**Table 2d. Energy levels of Re$^{4+}$ in the Zr site of ZrSiO$_4$[a]**

| Level | I.R.[b] | Energy (cm$^{-1}$) | Free ion state (%) | | | | |
|---|---|---|---|---|---|---|---|
| 1 | $\Gamma_7$ | 0 | 79 $^4F$ | + | 5 $^2D1$ | + | 5 $^2D2$ |
| 2 | $\Gamma_6$ | 2,152 | 68 $^4F$ | + | 8 $^2G$ | + | 8 $^2D2$ |
| 3 | $\Gamma_7$ | 5,444 | 87 $^4F$ | + | 8 $^4P$ | + | 1 $^2D2$ |
| 4 | $\Gamma_6$ | 6,299 | 71 $^4F$ | + | 8 $^4P$ | + | 8 $^2G$ |
| 5 | $\Gamma_6$ | 8,399 | 67 $^4F$ | + | 12 $^4P$ | + | 9 $^2G$ |
| 6 | $\Gamma_7$ | 9,023 | 74 $^4F$ | + | 10 $^2G$ | + | 5 $^4P$ |
| 7 | $\Gamma_6$ | 10,683 | 31 $^2G$ | + | 29 $^4F$ | + | 22 $^2H$ |
| 8 | $\Gamma_7$ | 12,346 | 25 $^4P$ | + | 24 $^4F$ | + | 17 $^2P$ |
| 9 | $\Gamma_7$ | 13,289 | 51 $^2G$ | + | 33 $^2H$ | + | 5 $^4F$ |
| 10 | $\Gamma_6$ | 13,703 | 37 $^2H$ | + | 36 $^2G$ | + | 12 $^4F$ |
| 11 | $\Gamma_7$ | 14,337 | 45 $^2H$ | + | 43 $^2G$ | + | 4 $^2D2$ |
| 12 | $\Gamma_6$ | 14,764 | 30 $^2G$ | + | 17 $^2H$ | + | 16 $^4P$ |
| 13 | $\Gamma_6$ | 18,666 | 26 $^4F$ | + | 23 $^4P$ | + | 21 $^2G$ |
| 14 | $\Gamma_7$ | 19,053 | 23 $^4F$ | + | 21 $^2H$ | + | 21 $^2G$ |
| 15 | $\Gamma_6$ | 19,848 | 27 $^2G$ | + | 24 $^2H$ | + | 19 $^4F$ |
| 16 | $\Gamma_7$ | 20,191 | 20 $^2H$ | + | 20 $^2G$ | + | 19 $^4P$ |
| 17 | $\Gamma_6$ | 21,395 | 28 $^2G$ | + | 27 $^2H$ | + | 12 $^2P$ |
| 18 | $\Gamma_7$ | 22,972 | 38 $^2G$ | + | 37 $^2H$ | + | 9 $^4F$ |
| 19 | $\Gamma_6$ | 23,777 | 30 $^2G$ | + | 24 $^2P$ | + | 17 $^2H$ |
| 20 | $\Gamma_7$ | 25,043 | 19 $^2H$ | + | 18 $^2F$ | + | 13 $^4F$ |
| 21 | $\Gamma_6$ | 26,288 | 26 $^2H$ | + | 19 $^4F$ | + | 18 $^2F$ |
| 22 | $\Gamma_6$ | 26,423 | 57 $^2H$ | + | 13 $^2F$ | + | 9 $^4F$ |
| 23 | $\Gamma_7$ | 26,682 | 27 $^2D2$ | + | 27 $^2H$ | + | 14 $^4F$ |
| 24 | $\Gamma_7$ | 27,662 | 32 $^4F$ | + | 28 $^2H$ | + | 15 $^2F$ |
| 25 | $\Gamma_6$ | 28,715 | 34 $^4F$ | + | 27 $^4P$ | + | 14 $^2F$ |
| 26 | $\Gamma_7$ | 29,226 | 38 $^4F$ | + | 17 $^2F$ | + | 16 $^4P$ |
| 27 | $\Gamma_7$ | 31,069 | 48 $^4F$ | + | 20 $^2F$ | + | 12 $^4P$ |
| 28 | $\Gamma_6$ | 31,233 | 67 $^4F$ | + | 10 $^2H$ | + | 8 $^4P$ |
| 29 | $\Gamma_7$ | 33,170 | 36 $^2F$ | + | 28 $^2D1$ | + | 13 $^4F$ |
| 30 | $\Gamma_6$ | 33,565 | 32 $^4P$ | + | 27 $^4F$ | + | 12 $^2H$ |
| 31 | $\Gamma_7$ | 34,774 | 75 $^4F$ | + | 7 $^4P$ | + | 6 $^2H$ |
| 32 | $\Gamma_6$ | 35,266 | 31 $^4F$ | + | 18 $^2G$ | + | 12 $^2D1$ |
| 33 | $\Gamma_6$ | 36,297 | 45 $^4F$ | + | 13 $^2D1$ | + | 13 $^4P$ |
| 34 | $\Gamma_6$ | 37,827 | 31 $^4P$ | + | 25 $^4F$ | + | 16 $^2H$ |
| 35 | $\Gamma_6$ | 38,248 | 46 $^4F$ | + | 15 $^2H$ | + | 12 $^2D1$ |
| 36 | $\Gamma_7$ | 38,303 | 39 $^4F$ | + | 20 $^4P$ | + | 12 $^2H$ |
| 37 | $\Gamma_7$ | 38,978 | 51 $^4P$ | + | 36 $^4F$ | + | 3 $^2H$ |
| 38 | $\Gamma_6$ | 39,715 | 30 $^2H$ | + | 18 $^4F$ | + | 17 $^4P$ |
| 39 | $\Gamma_7$ | 39,804 | 20 $^4P$ | + | 16 $^2H$ | + | 15 $^2D1$ |
| 40 | $\Gamma_7$ | 40,583 | 66 $^4P$ | + | 12 $^4F$ | + | 8 $^2H$ |
| 41 | $\Gamma_6$ | 41,378 | 27 $^4P$ | + | 20 $^2H$ | + | 20 $^4F$ |
| 42 | $\Gamma_7$ | 42,564 | 25 $^2G$ | + | 19 $^2H$ | + | 16 $^2F$ |
| 43 | $\Gamma_6$ | 45,152 | 53 $^2H$ | + | 18 $^2G$ | + | 10 $^2D2$ |
| 44 | $\Gamma_7$ | 45,917 | 33 $^2D2$ | + | 29 $^2G$ | + | 16 $^2H$ |
| 45 | $\Gamma_6$ | 46,436 | 28 $^2P$ | + | 26 $^2F$ | + | 20 $^4P$ |
| 46 | $\Gamma_7$ | 47,651 | 37 $^2H$ | + | 34 $^2F$ | + | 13 $^2G$ |
| 47 | $\Gamma_6$ | 48,165 | 40 $^2F$ | + | 30 $^2H$ | + | 14 $^2G$ |
| 48 | $\Gamma_7$ | 48,526 | 44 $^2F$ | + | 32 $^2H$ | + | 8 $^2G$ |
| 49 | $\Gamma_7$ | 49,045 | 42 $^2F$ | + | 27 $^2H$ | + | 19 $^2G$ |
| 50 | $\Gamma_6$ | 49,370 | 34 $^2F$ | + | 31 $^2H$ | + | 18 $^2G$ |

[a]The parameters are $F^{(2)} = 43,787$; $F^{(4)} = 29,340$; $\zeta = 3,741$; $B_{20} = -18,751$; $B_{40} = 3,669$; and $B_{44} = 34,779$ cm$^{-1}$.

[b]Irreducible representation of the double $D_{2d}$ group (Koster et al. 1963).

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## Table 3a. Energy levels of $W^{4+}$ in the Zr site in $Li_2ZrTeO_6$, cubic approximation[a]

| Level | I.R.[b] | Energy $(cm^{-1})$ | Free ion state (%) | | | | | |
|-------|---------|---------------------|--------|--------|--------|--------|--------|--------|
| 1 | $\Gamma_3$ | 0 | 83 $^3F$ | + | 11 $^3P$ | + | 3 $^1G$ | |
| 2 | $\Gamma_5$ | 184 | 81 $^3F$ | + | 13 $^3P$ | + | 4 $^1D$ | |
| 3 | $\Gamma_4$ | 4,362 | 82 $^3F$ | + | 17 $^3P$ | | | |
| 4 | $\Gamma_1$ | 5,052 | 73 $^3F$ | + | 20 $^3P$ | + | 3 $^1S$ | |
| 5 | $\Gamma_4$ | 10,778 | 50 $^1G$ | + | 42 $^1D$ | + | 6 $^3F$ | |
| 6 | $\Gamma_3$ | 11,007 | 51 $^1G$ | + | 42 $^1D$ | + | 3 $^3F$ | |
| 7 | $\Gamma_1$ | 22,265 | 47 $^1S$ | + | 44 $^1G$ | + | 8 $^3F$ | |
| 8 | $\Gamma_2$ | 45,682 | 99 $^3F$ | | | | | |
| 9 | $\Gamma_5$ | 46,344 | 96 $^3F$ | + | 2 $^3P$ | + | 1 $^1G$ | |
| 10 | $\Gamma_4$ | 47,582 | 93 $^3F$ | + | 3 $^3P$ | + | 2 $^1G$ | |
| 11 | $\Gamma_3$ | 47,618 | 90 $^3F$ | + | 8 $^3P$ | | | |
| 12 | $\Gamma_1$ | 52,080 | 79 $^3P$ | + | 18 $^3F$ | + | 2 $^1G$ | |
| 13 | $\Gamma_4$ | 52,909 | 76 $^3P$ | + | 17 $^3F$ | + | 5 $^1G$ | |
| 14 | $\Gamma_5$ | 53,365 | 49 $^3P$ | + | 21 $^1G$ | + | 18 $^1D$ | |
| 15 | $\Gamma_3$ | 55,652 | 76 $^3P$ | + | 22 $^3F$ | + | 1 $^1G$ | |
| 16 | $\Gamma_5$ | 57,965 | 35 $^3P$ | + | 34 $^1D$ | + | 24 $^1G$ | |
| 17 | $\Gamma_4$ | 58,884 | 91 $^1G$ | + | 5 $^3F$ | + | 2 $^3P$ | |

[a]The parameters are $F^{(2)} = 41,947$; $F^{(4)} = 28,071$; $\zeta = 3,102$; $B_{40} = -64,012$; and $B_{43} = (10/7)^{1/2} B_{40}$ $cm^{-1}$.

[b]Irreducible representations of the cubic O group (Koster et al, 1963).

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**Table 3b. Energy levels of $W^{4+}$ in the Zr site in $LiZrTeO_6$[a]**

| Level | I.R.[b] | Energy (cm$^{-1}$) | Free ion state (%) | | | | |
|---|---|---|---|---|---|---|---|
| 1 | $\Gamma_1$ | 0 | 82 $^3F$ | + | 13 $^3P$ | + | 3 $^1D$ |
| 2 | $\Gamma_{2,3}$ | 47 | 83 $^3F$ | + | 11 $^3P$ | + | 2 $^1D$ |
| 3 | $\Gamma_{2,3}$ | 788 | 80 $^3F$ | + | 12 $^3P$ | + | 4 $^1D$ |
| 4 | $\Gamma_{2,3}$ | 4,529 | 82 $^3F$ | + | 16 $^3P$ | | |
| 5 | $\Gamma_1$ | 5,065 | 82 $^3F$ | + | 17 $^3P$ | | |
| 6 | $\Gamma_1$ | 5,404 | 73 $^3F$ | + | 20 $^3P$ | + | 3 $^1S$ |
| 7 | $\Gamma_{2,3}$ | 10,360 | 50 $^1G$ | + | 41 $^1D$ | + | 6 $^3F$ |
| 8 | $\Gamma_{2,3}$ | 11,615 | 51 $^1G$ | + | 42 $^1D$ | + | 3 $^3F$ |
| 9 | $\Gamma_1$ | 11,732 | 51 $^1G$ | + | 42 $^1D$ | + | 5 $^3F$ |
| 10 | $\Gamma_1$ | 22,672 | 46 $^1S$ | + | 44 $^1G$ | + | 8 $^3F$ |
| 11 | $\Gamma_1$ | 45,897 | 99 $^3F$ | | | | |
| 12 | $\Gamma_{2,3}$ | 46,473 | 96 $^3F$ | + | 1 $^3P$ | + | 1 $^1G$ |
| 13 | $\Gamma_1$ | 46,680 | 94 $^3F$ | + | 4 $^3P$ | + | 1 $^1G$ |
| 14 | $\Gamma_1$ | 47,535 | 91 $^3F$ | + | 5 $^3P$ | + | 2 $^1G$ |
| 15 | $\Gamma_{2,3}$ | 47,776 | 90 $^3F$ | + | 7 $^3P$ | + | 1 $^1G$ |
| 16 | $\Gamma_{2,3}$ | 48,126 | 93 $^3F$ | + | 4 $^3P$ | + | 2 $^1G$ |
| 17 | $\Gamma_1$ | 52,319 | 78 $^3P$ | + | 18 $^3F$ | + | 2 $^1G$ |
| 18 | $\Gamma_{2,3}$ | 53,032 | 77 $^3P$ | + | 17 $^3F$ | + | 4 $^1G$ |
| 19 | $\Gamma_1$ | 53,452 | 45 $^3P$ | + | 23 $^1G$ | + | 19 $^1D$ |
| 20 | $\Gamma_1$ | 53,485 | 72 $^3P$ | + | 19 $^3F$ | + | 8 $^1G$ |
| 21 | $\Gamma_{2,3}$ | 53,769 | 49 $^3P$ | + | 22 $^1G$ | + | 17 $^1D$ |
| 22 | $\Gamma_{2,3}$ | 55,982 | 76 $^3P$ | + | 22 $^3F$ | + | 1 $^1G$ |
| 23 | $\Gamma_1$ | 58,009 | 38 $^3P$ | + | 32 $^1D$ | + | 21 $^1G$ |
| 24 | $\Gamma_{2,3}$ | 58,239 | 33 $^3P$ | + | 30 $^1G$ | + | 29 $^1D$ |
| 25 | $\Gamma_1$ | 58,821 | 88 $^1G$ | + | 6 $^3F$ | + | 4 $^3P$ |
| 26 | $\Gamma_{2,3}$ | 59,530 | 85 $^1G$ | + | 5 $^1D$ | + | 4 $^3F$ |

[a]The parameters are $F^{(2)} = 41,947$; $F^{(4)} = 28,071$; $\zeta = 3,102$; $B_{20} = 703.2$; $B_{40} = -61,733$; and $B_{43} = 77,440$ cm$^{-1}$.

[b]Irreducible representations of the $C_3$ group (Koster et al, 1963) ($\Gamma_{2,3} = \Gamma_2 + \Gamma_3$).

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# Appendix A.—Detailed X-Ray Data on 10 Host Materials

**Appendix A**

Contents

The following tables give the crystallographic and x-ray data on each of the 10 host materials discussed in the main body of text. The crystal-field components, $A_{nm}$, are calculated for the monopole (point charge), self-induced, and dipole contributions. Following each table is a list of references for that particular compound. These references include such topics as crystal growth, index of refraction, and electron spin resonance investigations. However, these reference lists are not, in any sense, extensive, and if further investigations are contemplated on any compound, additional literature searches should be undertaken.

# A-1. ZrSiO$_4$

## A-1.1   Crystallographic data on ZrSiO$_4$

Tetragonal $D_{4h}^{19}$ ($4_1/amd$), 141 (second setting)

| Ion | Site | Symmetry | $x$ | $y$ | $z$ | $q$ | $\alpha$ (Å$^3$) |
|------|------|----------|-----|-----|-----|-----|----------|
| Zr | $4a$ | $D_{2d}$ | 0 | 3/4 | 1/8 | 4 | 0.48[a] |
| Si | $4b$ | $D_{2d}$ | 0 | 1/4 | 3/8 | 4 | 0.03[a] |
| O | $16h$ | $C_s$ | 0 | $y$ | $z$ | -2 | 1.349[b] |

[a]*Fraga et al (1976).*
[b]*Schmidt et al (1979).*

## A-1.2   X-ray data

| $a$ (Å) | $c$ (Å) | $y$ | $z$ | Ref. |
|---------|---------|-----|-----|------|
| 6.6164 | 6.0150 | 0.067 | 0.198 | $a$ |
| 6.607 | 5.982 | 0.0661 | 0.1953 | $b$ |

[a]*Wyckoff (1968).*
[b]*Robinson et al (1971).*

## A-1.3   Crystal-field components, $A_{nm}$ (cm$^{-1}$/Å$^n$), for Zr ($D_{2d}$) site (x-ray data of Wyckoff)

| $A_{nm}$ | Monopole | Self-induced | Dipole | Total |
|----------|----------|--------------|--------|-------|
| $A_{20}$ | -12,765 | 349.4 | 33,644 | 21,229 |
| $A_{32}$ | -1,332 | 449.2 | 958.9 | '76.55 |
| $A_{40}$ | 910.3 | -1,130 | 524.3 | 304.5 |
| $A_{44}$ | 8,630 | -2,943 | -7,031 | -1,344 |
| $A_{52}$ | 6,142 | -2,379 | -1,796 | 1,967 |

## A-1.4   Crystal-field components, $A_{nm}$ (cm$^{-1}$/Å$^n$), for Zr ($D_{2d}$) site (Robinson et al data)

| $A_{nm}$ | Monopole | Self-induced | Dipole | Total |
|----------|----------|--------------|--------|-------|
| $A_{20}$ | -13,840 | 388.8 | 34,843 | 21,392 |
| $A_{32}$ | -522.2 | 332.7 | 754.3 | 564.8 |
| $A_{40}$ | 826.4 | -1,175 | 369.0 | 20.10 |
| $A_{44}$ | 9,024 | -3,114 | -7,316 | -1,406 |
| $A_{52}$ | 6,357 | -2,514 | -1.703 | 2,142 |

## A-1.5   $ZrSiO_4$ (zircon) references

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Di Gregario, S., M. Greenblatt, and J. H. Pifer (1980), ESR of $Nb^{4+}$ in zircon, Stat. Sol. **(b)101**, K149.

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# Appendix A

Schmidt, P. C., A. Weiss, and T. P. Das (1979), Effects of crystal-fields and self-consistency on dipole and quadruple polarization of closed shell ions, Phys. Rev. **B19**, 5525.

Silich, L. M., E. M. Kurpan, N. M. Bobkora, A. A. Stepanchuk, and S. A. Gailevich (1988), Quantitative x-ray phase analysis of ceramic in the $Al_2O_3$–$TiO_2$ system with $AlO_2$ and $ZrSiO_4$ added, Neorg. Mater. **24**, 1196.

Wyckoff, R. W. G. (1968), *Crystal Structures*, **4**, 157.

# A-2  $HfGeO_4$

## A-2.1  Crystallographic data on $HfGeO_4$

Tetragonal $C_{4h}^6$ $(I4_1/a)$, 88 (first setting), $Z = 4$

| Ion | Site | Symmetry | $x$ | $y$ | $z$ | $q$ | $\alpha$ $(\text{Å}^3)^b$ |
|-----|------|----------|-----|-----|-----|-----|------------|
| Hf  | $4b$ | $S_4$ | 0 | 0 | 1/2 | 4 | $0.57^a$ |
| Ge  | $4a$ | $S_4$ | 0 | 0 | 0 | 4 | $0.12^a$ |
| O   | $16f$ | $C_1$ | $x$ | $y$ | $z$ | $-2$ | $1.349^b$ |

[a]Fraga et al (1976).
[b]Schmidt et al (1979).

## A-2.2  X-ray data on $HfGeO_4$

| $a$ (Å) | $c$ (Å) | $x$ | $y$ | $z$ |
|---------|---------|-----|-----|-----|
| $4.849^a$ | 10.50 | 0.25 | 0.11 | 0.07 |
| $4.862^b$ | 10.497 | 0.2678 | 0.1739 | 0.0831 |

[a]Wyckoff (1968).
[b]Ennaciri et al (1986).

## A-2.3  Lattice sum, $A_{nm}$ $(\text{cm}^{-1}/\text{Å}^n)$, for Hf site $(S_4)$ (Wyckoff, 1968)

| $A_{nm}$ | Monopole | Self-induced | Dipole | Total |
|----------|----------|--------------|--------|-------|
| $A_{20}$ | 6,465 | $-662.8$ | $-13,794$ | $-7,992$ |
| $ReA_{32}$ | 3,527 | $-434.0$ | 4,855 | 7,948 |
| $ImA_{32}$ | 512.3 | $-45.50$ | 674.9 | 1,141 |
| $A_{40}$ | $-706.6$ | 389.5 | 3,039 | 2,721 |
| $ReA_{44}$ | $-2,525$ | 755.7 | 139.9 | $-1,629$ |
| $ImA_{44}$ | $-3,920$ | 961.5 | 2,154 | $-804.2$ |
| $ReA_{52}$ | 3,026 | $-966.8$ | $-9(.,1$ | 1,155 |
| $ImA_{52}$ | $-3,758$ | 1,289 | 2,735 | 267.2 |
| $|A_{44}|$ | 4,663 | — | — | 1,817 |

## A-2.4   HfGeO$_4$ references

Ennaciri, A., A. Kahn, and D. Michel (1986), Crystal structures of HfGeO$_4$ and ThGeO$_4$ germanates, J. Less-Common Metals, **124**, 105.

Fraga, S., J. Karwowski, and K. M. S. Saxena (1976), *Handbook of Atomic Data*, **5**, 319.

Schmidt, P. C., A. Weiss, and T. P. Das (1979), Effects of crystal-fields and self-consistency on dipole and quadrupole polarization of closed shell ions, Phys. Rev. **B19**, 5525.

Wyckoff, R. W. G. (1968), *Crystal Structures*, **3**, Interscience, New York, 21.

# A-3. $Li_2XTeO_6$ ($X$ = Zr, Hf)

## A-3.1 Crystallographic data on $Li_2XTeO_6$ ($X$ = Zr, Hf)

Trigonal $C_3^4$ ($R3$), 146 (hexagonal setting), $Z = 3$

| Ion | Site | Symmetry | $x$ | $y$ | $z$ | $q$ | $1.349^a$ |
|------|------|----------|-----|-----|-----|-----|-----------|
| Li1 | $3a$ | $C_3$ | 0 | 0 | $z$ | 1 | $0.0321^a$ |
| Li2 | $3a$ | $C_3$ | 0 | 0 | $z$ | 1 | $0.0321^a$ |
| $X$ | $3a$ | $C_3$ | 0 | 0 | $z$ | 4 | $\alpha_x^b$ |
| Te | $3a$ | $C_3$ | 0 | 0 | $z$ | 6 | $0.20^b$ |
| O1 | $9b$ | $C_1$ | $x$ | $y$ | $z$ | $-2$ | $1.349^a$ |
| O2 | $9b$ | $C_1$ | $x$ | $y$ | $z$ | $-2$ | $1.349^a$ |

$^a$Schmidt et al (1979).
$^b$Fraga et al (1976).

## A-3.2 X-ray data$^a$

| $X$ | $a$ (Å) | $c$ (Å) | $z_{Li1}$ | $z_{Li2}$ | $z_x$ | $z_{Te}$ | $x_{O1}$ | $y_{O1}$ | $z_{O1}$ |
|-----|---------|---------|-----------|-----------|-------|----------|----------|----------|----------|
| Zr | 5.172 | 13.847 | 0.29 | 0.76 | 0.993 | 0.500 | 0.049 | 0.355 | 0.077 |
| Hf | 5.164 | 13.782 | — | — | — | — | — | — | — |

| $X$ | $x_{O2}$ | $y_{O2}$ | $z_{O2}$ | $\alpha_x$ (Å$^3$) |
|-----|----------|----------|----------|--------------------|
| Zr | 0.652 | 0.962 | 0.576 | 0.48 |
| Hf | — | — | — | 0.57 |

$^a$Choisnet et al (1988).

## A-3.3 Lattice sum, $A_{nm}$ (cm$^{-1}$/Å$^n$), for Zr site ($C_3$)

| $A_{nm}$ | Monopole | Self-induced | Dipole | Total |
|----------|----------|--------------|--------|-------|
| $A_{10}$ | $-16,240$ | — | $-5,318$ | $-21,557$ |
| $A_{20}$ | 457.0 | 26.77 | 5,159 | 5,643 |
| $A_{30}$ | 2,319 | $-971.7$ | 5,941 | 7,289 |
| $RcA_{33}$ | 1,582 | $-239.1$ | $-5,242$ | $-3,899$ |
| $ImA_{33}$ | $-2,633$ | 881.9 | $-4,924$ | $-6,675$ |
| $A_{40}$ | $-14,546$ | 5,506 | 467.2 | $-8,573$ |
| $RcA_{43}$ | 3,925 | $-1,773$ | 9,713 | 11,865 |
| $ImA_{43}$ | 17,820 | $-6,293$ | $-4,997$ | 6,530 |
| $A_{50}$ | 1,239 | $-610.4$ | $-828.5$ | $-200.1$ |
| $RcA_{53}$ | 451.4 | $-38.55$ | $-1,981$ | $-1,568$ |
| $ImA_{53}$ | $-1,805$ | 1,241 | $-958.1$ | $-1,522$ |
| $|A_{43}|$ | 18,247 | — | — | 13,543 |

### A-3.4 Lattice sum, $A_{nm}$ (cm$^{-1}$/Å$^n$), for Hf site ($C_3$). [The positions of the ions within the unit cell are those of $Li_2ZrTeO_6$.]

| $A_{nm}$ | Monopole | Self-induced | Dipole | Total |
|---|---|---|---|---|
| $A_{10}$ | 68,052 | — | 9,798 | 77,850 |
| $A_{20}$ | 251.1 | 55.40 | 7,418 | 7,724 |
| $A_{30}$ | 2,387 | −998.3 | −28,186 | −26,797 |
| $ReA_{33}$ | 1,607 | −243.4 | 1,478 | 2,842 |
| $ImA_{33}$ | −2,677 | 903.0 | 21,103 | 19,330 |
| $A_{40}$ | −14,696 | 5,605 | 3,543 | −5,548 |
| $ReA_{43}$ | 3,972 | −1,811 | 11,185 | 13,345 |
| $ImA_{43}$ | 18,073 | −6,432 | −9,130 | 2,511 |
| $A_{50}$ | 1,249 | −617.3 | 4,789 | 5,421 |
| $ReA_{53}$ | 453.8 | −38.22 | −1,007 | −591.8 |
| $ImA_{53}$ | −1,834 | 1,270 | 4,337 | 3,773 |
| $|A_{43}|$ | 18,504 | — | — | 13,579 |

## A-3.5 $Li_2ZrTeO_6$ references

Choisnet, J., A. Rulmont, and P. Tarte (1988), Les tellurates mixtes $Li_2ZrTeO_6$ et $Li_2HfTeO_6$: un nouveau phénomène d'ordre dans la famille corindou, J. Solid State Chem. **75**, 124.

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Schmidt, P. C., A. Weiss, and T. P. Das (1979), Effects of crystal-fields and self-consistency on dipole and quadrupole polarization of closed shell ions, Phys. Rev. **B19**, 5525.

# A-4. $Li_6BeZrF_{12}$

## A-4.1  Crystallographic data on $Li_6BeZrF_{12}$

Tetragonal $D_{4h}^{19}$ ($I4_1/amd$), 141 (second setting), $Z = 4$

| Ion | Site | Symmetry | $x^a$ | $y$ | $z$ | $q$ | $\alpha\ (\text{Å}^3)^b$ |
|-----|------|----------|-------|-----|-----|-----|-----------|
| Be | $4a$ | $D_{2d}$ | 0 | 3/4 | 1/8 | 2 | 0.0125 |
| Zr | $4b$ | $D_{2d}$ | 0 | 1/4 | 3/8 | 4 | 0.480 |
| $Li_1$ | $8e$ | $C_{2v}$ | 0 | 1/4 | 0.1034 | 1 | 0.0321 |
| $Li_2$ | $16f$ | $C_2$ | 0.2303 | 0 | 0 | 1 | 0.0321 |
| $F_1$ | $16h$ | $C_s$ | 0 | 0.5340 | 0.4207 | –1 | 0.731 |
| $F_2$ | $16h$ | $C_s$ | 0 | 0.0260 | 0.2903 | –1 | 0.731 |
| $F_3$ | $16h$ | $C_s$ | 0 | –0.0568 | 0.0745 | –1 | 0.731 |

$^a$X-ray data:  $a = 6.570$, $c = 18.62$, Wyckoff (1968).

$^b$Schmidt et al (1979) except for Zr which is from Fraga et al (1976).

## A-4.2  Crystal-field components, $A_{nm}$ ($cm^{-1}/\text{Å}^n$), for Zr ($D_{2d}$) site

| $A_{nm}$ | Monopole | Self-induced | Dipole | Total |
|----------|----------|--------------|--------|-------|
| $A_{20}$ | 1,411 | 97.22 | –6,180 | –4,672 |
| $A_{32}$ | –3,101 | 763.4 | –4,360 | –6,697 |
| $A_{40}$ | –4,960 | 1,762 | –2,039 | –5,237 |
| $A_{44}$ | 5,393 | –1,943 | 3,955 | 7,405 |
| $A_{52}$ | 3,606 | –1,754 | 2,452 | 4,304 |

## A-4.3  $Li_6BeZrF_{12}$ references

Fraga, S., J. Karwowski, and K. M. S. Saxena (1976), *Handbook of Atomic Data*, **5**, 319.

Schmidt, P. C., A. Weiss, and T. P. Das (1979), Effects of crystal-fields and self-consistency on dipole and quadrupole polarization of closed shell ions, Phys. Rev. **B19**, 5525.

Wyckoff, R. W. G. (1968), *Crystal Structures*, Vol. **4**, Interscience, New York, 57.

# A-5. ZrGeO$_4$

## A-5.1 Crystallographic data on ZrGeO$_4$

Tetragonal $C_{4h}^6$ ($I4_1/a$), 88 (first setting), $Z = 4$

| Ion | Site | Symmetry | $x^a$ | $y$ | $z$ | $q$ | $\langle r \rangle^b$ |
|-----|------|----------|-------|-----|-----|-----|---------|
| Ge | $4a$ | $S_4$ | 0 | 0 | 0 | 4 | 0 |
| Zr | $4b$ | $S_4$ | 0 | 0 | 1/2 | 4 | 0 |
| O | $16f$ | $C_1$ | $x$ | $y$ | $z$ | –2 | 1 |

$^a$X-ray data: $u = 4.8660$, $c = 10.55$ (Å), $x = 0.2664$, $y = 0.1726$, $z = 0.0822$ (Ennaciri et al, 1984).
$^b$Fraga et al (1976).

## A-5.2 Crystal-field components, $A_{nm}$ (cm$^{-1}$/Å$^n$), for Zr ($S_4$) site

| $A_{nm}$ | Monopole | Self-induced | Dipole | Total |
|----------|----------|--------------|--------|-------|
| $A_{20}$ | 5,175 | –202 | –13,444 | –8,470 |
| $\mathrm{Re}A_{32}$ | –2,584 | 543 | 3,702 | 1,661 |
| $\mathrm{Im}A_{32}$ | 5,083 | –1,228 | 2,074 | 5,928 |
| $A_{40}$ | –6,023 | 1,773 | 7,119 | 2,870 |
| $\mathrm{Re}A_{44}$ | –5,668 | 1,928 | –154 | –3,894 |
| $\mathrm{Im}A_{44}$ | –4,887 | 1,457 | 50 | –3,380 |
| $\mathrm{Re}A_{52}$ | 1,982 | –754 | 394 | 1,622 |
| $\mathrm{Im}A_{52}$ | –5,705 | 2,280 | 717 | –2,708 |
| $|A_{44}|$ | 7,484 | — | — | 5,516 |

## A-5.3 Crystal-field components, $A_{nm}$ (cm$^{-1}$/Å$^n$), for Ge ($S_4$) site in ZrGeO$_4$

| $A_{nm}$ | Monopole | Self-induced | Dipole | Total |
|----------|----------|--------------|--------|-------|
| $A_{20}$ | –16,423 | 2,648 | –17,512 | –31,288 |
| $\mathrm{Re}A_{32}$ | 17,821 | –5,603 | 8,684 | 20,902 |
| $\mathrm{Im}A_{32}$ | 36,558 | –12,128 | 21,800 | 46,235 |
| $A_{40}$ | –16,132 | 7,646 | –3,565 | –12,051 |
| $\mathrm{Re}A_{44}$ | –10,322 | 5,533 | –6,628 | –11,417 |
| $\mathrm{Im}A_{44}$ | 12,115 | –6,078 | 9,726 | 15,764 |
| $\mathrm{Re}A_{52}$ | –2,489 | 1,770 | –3,199 | –3,918 |
| $\mathrm{Im}A_{52}$ | –5,540 | 3,989 | –6,510 | –8,062 |
| $|A_{44}|$ | 15,916 | — | — | 19,464 |

## A-5.4 $ZrGeO_4$ references

Ennaciri, A., A. Kahn, and D. Michel (1986), Crystal structures of $HfGeO_4$ and $ThGeO_4$ germanates, J. Less-Common Metals, **124**, 105.

Fraga, S., J. Karwowski, and K. M. S. Saxena (1976), *Handbook of Atomic Data*, **5**, 319.

Schmidt, P. C., A. Weiss, and T. P. Das (1979), Effects of crystal-fields and self-consistency on dipole and quadrupole polarization of closed shell ions, Phys. Rev. **B19**, 5525.

# A-6. $Zr_3GeO_8$

## A-6.1  Crystallographic data on $Zr_3GeO_8$

Tetragonal $D_{2d}^{11}$ ($1\bar{4}2m$), 121 (first setting), $Z = 2$

| Ion | Site | Symmetry | $x^a$ | $y$ | $z$ | $q$ | $\alpha$ $(\text{Å}^3)^b$ |
|-----|------|----------|-------|-----|-----|-----|---------|
| Ge | $2a$ | $D_{2d}$ | 0 | 0 | 0 | 4 | $0.12^b$ |
| $Zr_1$ | $2b$ | $D_{2d}$ | 0 | 0 | 1/2 | 4 | $0.48^b$ |
| $Zr_2$ | $4d$ | $S_4$ | 0 | 1/2 | 1/4 | 4 | $0.48^b$ |
| $O_1$ | $8i$ | $C_s$ | 0.2004 | 0.2004 | 0.3410 | -2 | $1.349^c$ |
| $O_2$ | $8i$ | $C_s$ | 0.2170 | 0.2170 | 0.0904 | -2 | $1.349^c$ |

$^a$X-ray data: $a = 5.005$, $c = 10.550$ (Å), Ennaciri et al (1984).
$^b$Fraga et al (1976).
$^c$Schmidt et al (1979).

## A-6.2  Crystal-field components, $A_{nm}$ ($cm^{-1}/\text{Å}^n$), for Ge ($D_{2d}$) site

| $A_{nm}$ | Monopole | Self-induced | Dipole | Total |
|----------|----------|--------------|--------|-------|
| $A_{20}$ | -9,412 | 1,462 | -13,999 | -21,949 |
| $A_{32}$ | 37,705 | -11,897 | 26,755 | 52,564 |
| $A_{40}$ | -17,256 | 7,914 | -7,401 | -16,742 |
| $A_{44}$ | 13,709 | -6,580 | 10,516 | -17,644 |
| $A_{52}$ | -3,458 | 2,382 | -5,316 | -6,393 |

## A-6.3  Crystal-field components, $A_{nm}$ ($cm^{-1}/\text{Å}^n$), for $Zr_1$ ($D_{2d}$) site

| $A_{nm}$ | Monopole | Self-induced | Dipole | Total |
|----------|----------|--------------|--------|-------|
| $A_{20}$ | 10,659 | -900 | -7,933 | 1,827 |
| $A_{32}$ | 300.1 | 38.3 | -98.4 | 240.6 |
| $A_{40}$ | -7,875 | 2,384 | 6,546 | 1,055 |
| $A_{44}$ | 6,875 | -2,024 | -91.5 | 4,760 |
| $A_{52}$ | -5,795 | 2,320 | -289.0 | -3,764 |

### A-6.4 Crystal-field components, $A_{nm}$ (cm$^{-1}$/Å$^n$), for Zr$_2$ ($S_4$) site of Zr$_3$GeO$_8$

| $A_{nm}$ | Monopole | Self-induced | Dipole | Total |
|---|---|---|---|---|
| $A_{20}$ | −7,440 | 974 | −6,987 | −13,453 |
| Re$A_{32}$ | −6,953 | 1,611 | 129 | −5,219 |
| Im$A_{32}$ | −12,700 | 3,350 | −5,948 | −15,298 |
| $A_{40}$ | −9,538 | 2,874 | 3,317 | −3,347 |
| Re$A_{44}$ | −6,213 | 2,229 | −170 | −4,154 |
| Im$A_{44}$ | 6,389 | −2,090 | 2,204 | 6,500 |
| Re$A_{52}$ | 1,489 | −645 | 1,029 | 1,873 |
| Im$A_{52}$ | 3,755 | −1,660 | 1,473 | 3,568 |
| $|A_{44}|$ | 8,910 | — | — | 7,714 |

### A-6.5 Zr$_3$GeO$_8$ references

Ennaciri, A., A. Kahn, and D. Michel (1986), Crystal structures of HfGeO$_4$ and ThGeO$_4$ germanates, J. Less-Common Metals, **124**, 105.

Fraga, S., J. Karwowski, and K. M. S. Saxena (1976), *Handbook of Atomic Data*, **5**, 319.

Schmidt, P. C., A. Weiss, and T. P. Das (1979), Effects of crystal-fields and self-consistency on dipole and quadrupole polarization of closed shell ions, Phys. Rev. **B19**, 5525.

# A-7. ThSiO₄

## A-7.1 Crystallographic data on ThSiO₄

Tetragonal $D_{4h}^{19}$ ($I4_1/amd$), 141 (first setting), $Z = 4$

| Ion | Site | Symmetry | $x^a$ | $y$ | $z$ | $q$ | $\alpha$ (Å³) |
|------|------|----------|-------|--------|--------|----|----------------|
| Th | $4a$ | $D_{2d}$ | 0 | 3/4 | 1/8 | 4 | 1.52[b] |
| Si | $4b$ | $D_{2d}$ | 0 | 3/4 | 5/8 | 4 | 0.030[b] |
| O | $16h$ | $C_s$ | 0 | 0.0732 | 0.2104 | −2 | 1.349[c] |

[a]X-ray data: $a = 7.1328$ Å, $c = 6.3188$ Å, Taylor et al (1978).
[b]Fraga et al (1976).
[c]Schmidt et al (1979).

## A-7.2 Crystal-field components, $A_{nm}$ (cm⁻¹/Åⁿ), for Th site ($D_{2d}$)

| $A_{nm}$ | Monopole | Self-induced | Dipole | Total |
|----------|----------|--------------|--------|-------|
| $A_{20}$ | −6,300 | −141.4 | 26,500 | 20,058 |
| $A_{32}$ | −1,653 | 193.5 | 1,666 | 206.2 |
| $A_{40}$ | 18.45 | −493.3 | 1,350 | 875.4 |
| $A_{44}$ | 4,906 | −1,316 | −4,142 | −552.9 |
| $A_{52}$ | 3,753 | −1,108 | −1,116 | 1,529 |

## A-7.3 Crystal-field components, $A_{nm}$ (cm⁻¹/Åⁿ), for Si site ($D_{2d}$)

| $A_{nm}$ | Monopole | Self-induced | Dipole | Total |
|----------|----------|--------------|--------|-------|
| $A_{20}$ | 7,634 | −3,788 | 28,562 | 32,408 |
| $A_{32}$ | −64,599 | 24,940 | −45,571 | −85,230 |
| $A_{40}$ | −35,517 | 21,569 | −31,618 | −46,566 |
| $A_{44}$ | 13,907 | −9,471 | 10,306 | 14,741 |
| $A_{52}$ | −7,113 | 6,834 | −14,295 | −14,573 |

## A-7.4 ThSiO$_4$ references

Fraga, S., J. Karwowski, and K. M. S. Saxena (1976), *Handbook of Atomic Data*, **5**, 319.

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# A-8. ThGeO$_4$

## A-8.1 Crystallographic data on ThGeO$_4$

Tetragonal $D_{4h}^{19}$ ($I4_1/amd$), 141 (first setting), $Z = 4$

| Ion | Site | Symmetry | $x$ | $y$ | $z$ | $q$ | $\alpha$ (Å$^3$) |
|-----|------|----------|-----|-----|-----|-----|------------------|
| Th | 4$a$ | $D_{2d}$ | 0 | 0 | 0 | 4 | 1.52[b] |
| Ge | 4$b$ | $D_{2d}$ | 0 | 0 | 1/2 | 4 | 0.12[b] |
| O | 16$h$ | $C_s$ | 0 | 0.1803[a] | 0.3214 | −2 | 1.349[c] |

[a]$X$-ray data: $a = 7.230$ Å, $c = 6.539$ Å, Ennaciri et al (1986).
[b]Fraga et al (1976).
[c]Schmidt et al (1979).

## A-8.2 Tetragonal $C_{4h}^6$ ($I4_1/a$), 88 (first setting), $Z = 4$

| Ion | Site | Symmetry | $x$ | $y$ | $z$ | $q$ | $\alpha$ (Å$^3$) |
|-----|------|----------|-----|-----|-----|-----|------------------|
| Th | 4$b$ | $S_4$ | 0 | 0 | 1/2 | 4 | 1.52[b] |
| Ge | 4$b$ | $S_4$ | 0 | 0 | 0 | 4 | 0.12[b] |
| O | 16$f$ | $C_1$ | 0.2548[a] | 0.1493 | 0.0787 | −2 | 1.348[c] |

[a]$X$-ray data: $a = 5.145$ Å, $c = 10.531$ Å, Ennaciri et al (1986).
[b]Fraga et al (1976).
[c]Schmidt et al (1979).

## A-8.3 Crystal-field components, $A_{nm}$ (cm$^{-1}$/Å$^n$), for Th site ($D_{2d}$)

| $A_{nm}$ | Monopole | Self-induced | Dipole | Total |
|----------|----------|--------------|--------|-------|
| $A_{20}$ | −8,188 | 49.52 | 21,620 | 13,482 |
| $A_{32}$ | 151.6 | −68.33 | 171.6 | 254.8 |
| $A_{40}$ | 549.2 | −547.2 | 448.5 | 450.6 |
| $A_{44}$ | 5,368 | −1,397 | −3,701 | 270.1 |
| $A_{52}$ | −3,634 | 1,074 | 829.8 | −1,730 |

## A-8.4 Crystal-field components, $A_{nm}$ (cm$^{-1}$/Å$^n$), for Ge site ($D_{2d}$)

| $A_{nm}$ | Monopole | Self-induced | Dipole | Total |
|---|---|---|---|---|
| $A_{20}$ | 15,677 | −3,858 | 19,380 | 31,119 |
| $A_{32}$ | 48,087 | −15,117 | 27,015 | 59,985 |
| $A_{40}$ | −26,107 | 12,492 | −17,436 | −31,051 |
| $A_{44}$ | 8,289 | −4,775 | 5,642 | 9,156 |
| $A_{52}$ | 7,228 | −5.656 | 8,759 | 10,331 |

## A-8.5 Crystal-field components, $A_{nm}$ (cm$^{-1}$/Å$^n$), for Th site ($S_4$)

| $A_{nm}$ | Monopole | Self-induced | Dipole | Total |
|---|---|---|---|---|
| $A_{20}$ | 3,593 | −382.9 | −4,985 | −1,775 |
| Re$A_{32}$ | 1,850 | −150.2 | 3,916 | 5,616 |
| Im$A_{32}$ | −98.96 | 33.57 | 124.6 | 59.21 |
| $A_{40}$ | −3,236 | 977.3 | 3,822 | 1,563 |
| Re$A_{44}$ | −3,857 | 977.1 | 1,069 | −1,811 |
| Im$A_{44}$ | −3,787 | 888.8 | 810.3 | −2,088 |
| Re$A_{52}$ | 1,923 | −599.4 | 138.0 | 1,461 |
| Im$A_{52}$ | −3,970 | 1,326 | 1,369 | −1,275 |
| $|A_{44}|$ | 5,405 | — | — | 2,764 |

## A-8.6 Crystal-field components, $A_{nm}$ (cm$^{-1}$/Å$^n$), for Ge site ($S_4$)

| $A_{nm}$ | Monopole | Self-induced | Dipole | Total |
|---|---|---|---|---|
| $A_{20}$ | −21,877 | 3,538 | −13,762 | −32,101 |
| Re$A_{32}$ | 22,842 | −7,897 | 15,609 | 30,554 |
| Im$A_{32}$ | 40,279 | −13,830 | 23,195 | 49,644 |
| $A_{40}$ | −16,030 | 8,434 | −7,823 | −15,419 |
| Re$A_{44}$ | −9,474 | 5,340 | −3,575 | −7,709 |
| Im$A_{44}$ | 16,075 | −8,588 | 13,046 | 20,533 |
| Re$A_{52}$ | −3,667 | 2,846 | −4,027 | −4,849 |
| Im$A_{52}$ | −6,414 | 5,096 | −5,729 | −7,048 |
| $|A_{44}|$ | 18,659 | — | — | 21,932 |

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